Available online at www.sciencedirect.com

SciVerse ScienceDirect

Energy Procedia 17 (2012) 1050 – 1056

Energy Procedia

2012 International Conference on Future Electrical Power and Energy Systems

Performence of Fe-Mn Oxide Sorbent by Doping with Rare-Earth Oxides

Hai Zhao, Youning Xu,Junqing Liu

Department of Energy and Power Engineering, Shenyang Institute of Engineering Liaoning, China

Abstract

To develop a highly active COS sorbent, Fe–Mn mixed oxide doped with La and Sm were studied. The effects of promoters on the Fe–Mn oxides were investigated by XRD, BET and other methods. XRD results revealed that the degree of crystallinity and particle size of Fe–Mn oxide phase decreased due to doping with La2O3 and Sm2O3. Addition of rare-earth oxides led to a progressive increase in the surface area of the sample. Desulfurization tests showed that the addition of 3 wt % La2O3 and Sm2O3 greatly improved the absorption sulfur capacity of the sorbent for COS removal.

Keywords: Fe-Mn oxide; COS removal; Doping; La2O3; Sm2O3

1.Introduction

Recently, many developed countries have been researching techniques for the use of coal as clean energy such as the Integrated Gasification Combined Cycle (IGCC). To better utilize the technology, the removal of pollutants such as H_2S and COS from coal-derived gas is necessary. If H2S and COS concentration is reduced to less than 20 ppm such a process may be used with the IGCC, and if reduced to less than 1 ppm the gas can be used with fuel cells. Synthesis gases used in catalytic processes must usually be almost sulfur-free because some synthesis catalysts are extremely sensitive to sulfur poisoning[1-6].

H_2S is easily removed by metal oxides. On the contrary, the removal of COS is rather difficult since COS is rather inactive due to its neutrality. Many kinds of metal oxides or mixed metal oxides have been examined as candidate solids for COS removal such as Zn, Ca, Mn, and Fe. Among them, Zinc oxide is more attractive because of its favorable sulfidation thermodynamics and high sulfur capacity. Calcium oxide is thermodynamically a good sorbent for COS removal from hot fuel gases. From an economic

 doi:10.1016/j.egypro.2012.02.206

point of view, iron oxide is more attractive than others in that it has high capacity and reactivity. Also, manganese-based sorbent can remove H_2S and COS simultaneously. For these reasons, many efforts have been drawn to remove COS from gas using iron oxide or manganese oxide. In order to develop an efficient sorbent for COS removal, however, more studies are needed.

In this paper, La_2O_3 and Sm_2O_3 were selected as the promoters among the Fe–Mn mixed oxide sorbent for COS removal from syngas. The aim is to investigate the desulfurization performance of the mixed oxides sorbent by adding small amounts of rare-earth oxides. The effects of these promoters on the surface and structural properties of Fe–Mn oxide are studied with the objective to explain the differences in desulfurization behaviors.

2.Experimental

Fe–Mn oxide sorbent was prepared by coprecipitation method. $Fe(NO_3)_3$ and $Mn(NO_3)_2$ were dissolved in deionized water (Fe/Mn in molar ratio =1:0.2). This mixture and Na_2CO_3 solution (1.0 mol/L) were simultaneously added dropwise into a flask containing 50 mL of water at 70 °C under vigorous stirring. The pH was controlled at 8.0 by varying their addition rate. After coprecipitation occurred, the solution containing the precipitated product was maintained at 70 °C with stirring for 1 h. Further, the product was filtered and washed several times with deionized water to eliminate the sodium ions, then was dried at 80 °C for 16 h.

The doped solid samples were prepared with the same method with solutions containing different amounts of $La(NO_3)_3$ or $Sm(NO_3)_3$. All precursors were crushed and ground to a powder of 200 mesh. Distilled water was added to make this powder into sorbent slurry forms and extruded in a syringe to cylindrical shapes. The extrudates were dried overnight at 80 °C and then calcined in air in a muffle furnace at 500 °C for 4 h.

XRD study was carried out using a Rigaku D/max-rA 12KW powder X-ray diffractometer with a scanning range from 10º to 80º and a Nickel-filtered Cu Kα radiation source at 40 kV and 100 mA. The mean crystallite size of the cubic phase was calculated from the Scherrer equation, where the Scherrer constant (particle shape factor) was taken as 0.89.

BET analyses were performed with a Micromeritics ASAP 2010 instrument. The surface areas of samples were determined from nitrogen adsorption isotherms measured at -196 ℃. The experimental error for textural properties is considered less than ±5%.

Desulfurization tests were performed in a fixed-bed quartz reactor with a diameter of 1.2 cm placed in an electric furnace. Three gram of sorbent was packed into the reactor, working at atmospheric pressure and the space velocity was maintained at 1000 h^{-1}. COS concentration in the exit gas was measured on-line, using a quadrupole mass spectrometry. Data from runs at 325 °C were presented here, using a gas of composition 65 vol.% H_2 , 25 vol.% CO, 5 vol.% CO_2, 1.5 vol.% COS, balance N_2, and was considered to be completed until the COS concentration of the outlet was 50 mg/m^3.

3.Results and Discussion

X-ray diffractograms of the samples

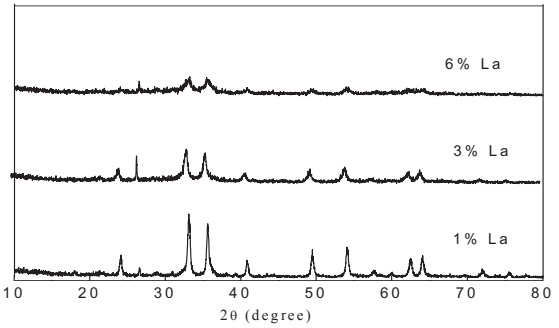

Figure 1. X-ray diffractograms of Fe–Mn based sorbents with various loadings of La

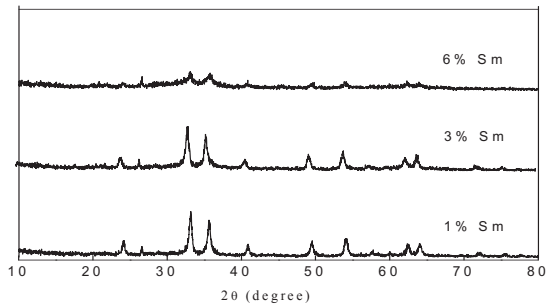

Figure 2. X-ray diffractograms of Fe–Mn based sorbents with various loadings of Sm

The crystalline phases of Fe–Mn oxide and doped mixed solids calcined at 500 °C were determined from XRD measurements. X-ray diffractograms of Fe–Mn oxide sorbent and different rare–earth oxides doped samples are given in Figure 1 and Figure 2. Figures reveal that Fe–Mn mixed solids employed in the investigation consisted of the well-crystallized α-Fe_2O_3 phase. The peaks characterizing of manganese oxide could be hardly detected. This indicates that manganese may be in a high dispersion degree due to low content or small crystal size. Inspection of Figures shows that, the absence of diffraction line of La_2O_3 or Sm_2O_3 phase in the samples suggests its presence in an amorphous state. The absence of the diffraction lines of La_2O_3 or Sm_2O_3 phase in the doped solids might suggest the existence of very fine particles of La_2O_3 or Sm_2O_3 whose crystallite size became very small. Also, the absence of dopant oxides as separate phases might result from their dissolution in ferric-manganese oxide lattice.

The peak heights of diffraction lines of Fe_2O_3 phases for pure and doped samples were determined and plotted in Figure 3.

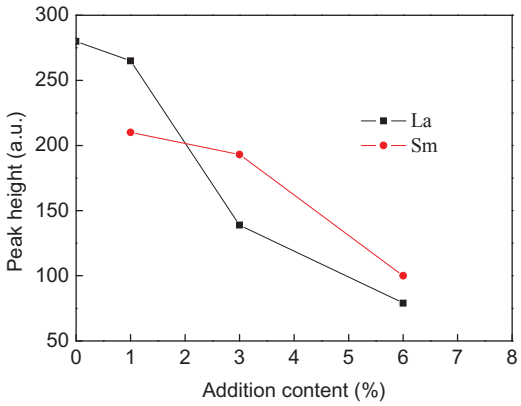

Figure 3. Effect of rare-earth oxide doping on the heights of diffraction lines of Fe_2O_3 phase for Fe–Mn mixed oxide solids

Figure 3 shows that the height of the main diffraction lines (at d = 2.70 Å) of Fe_2O_3 present in Fe–Mn oxide sorbent attained 280 a.u. The value measured was 79 a.u. for the solids doped with 6% La_2O_3, and 100 a.u. for 6% Sm2O3. Furthermore, the crystallite size of the Fe_2O_3 phase present in pure sample calcined at 500 °C measured 150 Å and decreased to 110 Å and 112 Å for the samples doped with 6.0% La_2O_3 and Sm_2O_3, respectively.

It is found that doping of Fe–Mn oxide solids with small amounts of La_2O_3 or Sm_2O_3 resulted in a decrease in the peak height of diffraction lines of Fe_2O_3 phase. The results indicate that the values of mean crystallite sizes of the particles are decreased by the addition of La_2O_3 and Sm_2O_3. Also, the formation of small sized crystallites increases the degree of dispersion of Fe–Mn oxide solids. The observed changes in the degree of crystallinity and particle size of Fe_2O_3 phase due to the doping of rare-earth oxides are expected to modify the structural properties and desulfurization performances of the Fe–Mn oxide sorbent.

BET study of the samples

The different surface characteristics of pure and variously doped solids were determined from nitrogen adsorption isotherms conducted at −196 ℃. The data obtained are given in Figure 4.

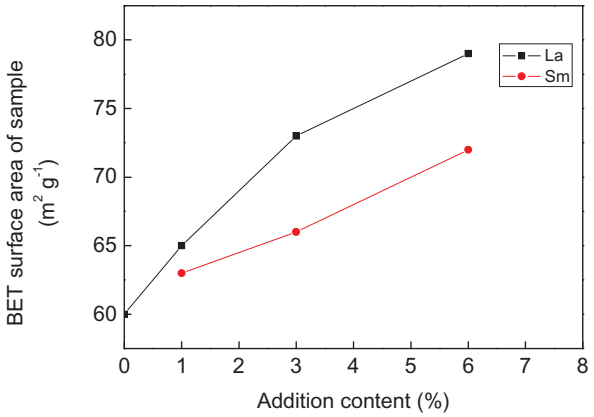

Figure 4. Effect of rare-earth oxide doping on surface area for Fe–Mn mixed oxide solids

Figure 4 illustrated that addition of rare-earth oxide alters the BET area of the sorbent. The samples doped with La_2O_3 or Sm_2O_3 brought about a progressive increase in its surface areas. The increase in the BET of solids could be attributed to the effective observed decrease in the crystallite size of iron oxide (manganese oxide). It is seen from this Figure that rare earth oxides doped followed by calcination at 500 °C resulted in significant increases in their BET to an extent proportional to the amount of rare earth oxides added.

The significant decrease in the particle size of Fe–Mn oxide solids and the increase in its surface area due to doping with La_2O_3 and Sm_2O_3 are expected to modify the desulfurization properties of the sorbent.

Desulfurization tests of the sorbents

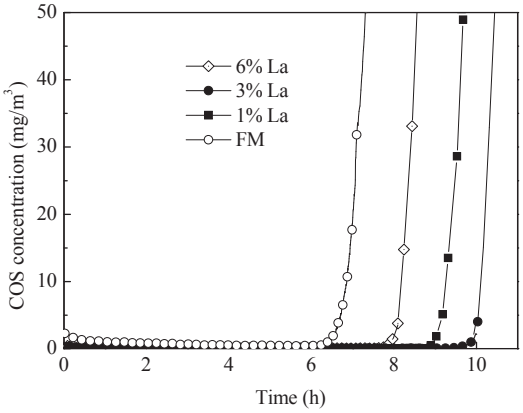

Figure 5. COS breakthrough curves of Fe–Mn based sorbents with various loadings of La promoter

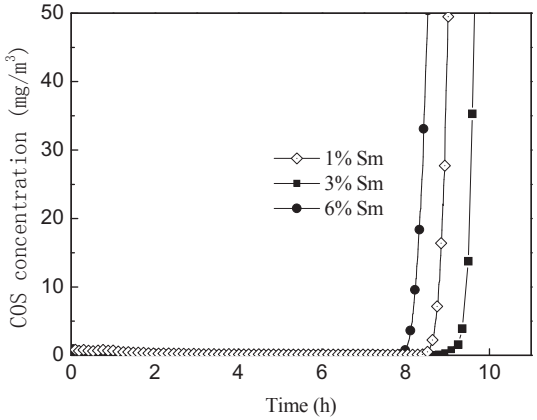

Figure 6. COS breakthrough curves of Fe–Mn based sorbents with various loadings of Sm promoter

Figures show the COS breakthrough curves of various sorbents at 325 °C and space velocity of 1000 h^{-1}. Fe–Mn mixed oxide sorbent shows a breakthrough time for about 7 h, the doping of Fe–Mn oxide solid with La_2O_3 and Sm_2O_3 results in a progressive increase in the breakthrough time. It was found that 3% of La or Sm should be added to the solid sample and the sorbent doped with 3% La_2O_3 shows the maximum increase in the breakthrough time. The increase in the amounts of Sm or La added to the pure sample from 3 to 6% will result in a decrease in sulfur capacity.

The increase in the desulfurization performance of sorbents due to the addition of Sm_2O_3 and La_2O_3 could be an effective increase in the concentration of desulfurization active sites which taking part in the absorption process. The observed changes in the desulfurization activity of doped sample solids could result from the induced changes in their surface areas and a decrease in their particle size leading to a decrease in the degree of crystallinity. It is showed that proper amounts of promoters play a positive role in desulfurization reactions for COS removal. However, excess amounts of La_2O_3 and Sm_2O_3 led to an enrichment on the surface of Fe–Mn oxide solids which lead to a lower effective active surface towards COS removal and that is responsible for observed decrease in its desulfurization activity when excess amount of rare-earth oxide solids were added to the pure sample.

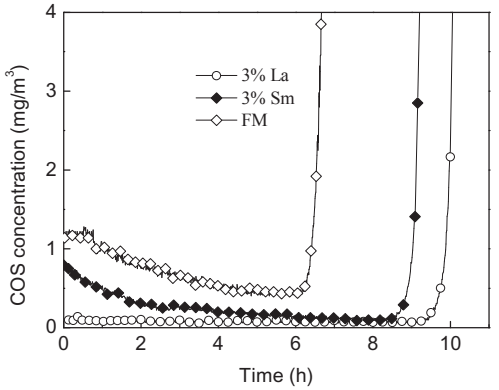

Figure 7. COS breakthrough curves of pure sample and different rare-earth oxide doped samples (expanded scale)

The expanded scale COS breakthrough curves of pure sample and different rare-earth oxide doped samples were shown in Figure 7. It is found that the pure sample shows the lowest desulfurization efficiency. Among them, the desulfurization efficiency of the La-promoted sorbent is higher than those of Sm-doped samples. Results suggest that La or Sm play an important positive role in increasing the sorbent sulfur capacity, while sorbent added with La additive shows better COS removal efficiency than Sm doping. Probably the promoters may be not only play the role of structural promoter but also the electronic promoter in desulfurization reactions.

4.Conclusions

The following conclusions are drawn from this work.

- To develop a highly useful COS removal sorbent, a modification of Fe–Mn oxide by adding rare-earth oxides was studied. The doping of iron oxide and manganese oxide solids with rare-earth oxides resulted in an effective decrease in the degree of crystallinity of iron oxide phase and its particle size.
- The surface area of Fe–Mn oxide sample was found to increase progressively by increasing the amount of dopant added.
- The promoters played an important role in the COS removal from syngas. The increase of the amount of La_2O_3 and Sm_2O_3 from 1 to 3% added to the FM solids brought about an increase in sulfur capacity. The sulfur capacity increase was more pronounced in case of La_2O_3 doping. Opposite effect was observed by increasing the La or Sm content from 3 to 6%.

Acknowlegement

The authors thank Major State Basic Research Development Program of China for financial support for this work under Project No.2005CB221203.

。References

[1] Ruth, LA., Vision 21: Fossil fuel-based energy for the 21st century. Proceeding of workshop on clean energy utilization technology, Seoul, Korea; 2001.

[2] Eiji Sasaoka, Tomoo Ichio and Shigeaki Kasaoka. High-Temperature H_2S Removal from Coal-Derived Gas by Iron ore. Energy & Fuels 1992, 6, 603-608.

[3] B. Peter Williamsa, Nicola C. Younga, John Westb, Colin Rhodesb, Graham J. Hutchingsb, C.N. Satterfield, Carbonyl sulphide hydrolysis using alumina catalysts Heterogeneous Catalysis in Industrial Practice, McGraw-Hill, New York, 1991, p. 378.

[4] Federal Energy Technology Center. Vision 21 program plan: clean energy plants for the 21th century. FETC office of Fossil Energy, US Department of Energy; 1999.

[5] Lee,A.L. Internal Reforming Development for Solid Oxide fuel Cells-Final Report; Department of Energy Report MC/220045-2364; U.S. Government Printing Offece: Washington, DC, 1987.

[6] Kazuo Taniguchi，Md. Azhar Uddin， Shigeru Hirano，et al., Characterization of Reaction between ZnO and COS [J]. Eng. Chem. Res. 1996，35：2389-2394.